SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*   ARO 13435.5-CH; 16357.9-CH

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM	
1 REPORT NUMBER	2 GOVT ACCESSION NO. AD-A130022	3 RECIPIENT'S CATALOG NUMBER
4 TITLE *(and Subtitle)* The Structure of Polyurethane Elastomers	5 TYPE OF REPORT & PERIOD COVERED Final 3/1/76 - 9/30/82	
	6 PERFORMING ORG. REPORT NUMBER	
AUTHOR(s) John Blackwell Professor of Macromolecular Science	8 CONTRACT OR GRANT NUMBER(s) DAAG29 76G 0152 DAAG29 76C 0070	
PERFORMING ORGANIZATION NAME AND ADDRESS Case Western Reserve University Cleveland, Ohio 44106	10 PROGRAM ELEMENT. PROJECT, TASK AREA & WORK UNIT NUMBERS	
CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE 6/14/83	
	13 NUMBER OF PAGES 23	
MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)* U.S. Army Research Office P.O. Box 12211 Research Triangle Park NC 27709	15 SECURITY CLASS. *(of this report)* Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

JUL 1 1983

17 DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

NA

18 SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19 KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Polyurethane, Elastomer, Block Copolymer

X-ray Diffraction, Conformation, Structure-Property Relationships

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Polyurethane elastomers derive their properties from phase separation into hard (urethane) and soft (polyether or polyester) domains. We have used x-ray diffraction and conformational analysis to determine the structure of the hard domains in MDI/diol/polyester polyurethanes. A new structure has been developed for MDI/butandiol (C_4) hard segments, based on the following approaches. Solution of structures of two MDI derivatives showed the basic features of the polymer conformation, packing, and hydrogen bonding. Better

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

83 06 30 108

DTIC FILE COPY
AD A130022

20. ABSTRACT CONTINUED

quality x-ray patterns allowed determination of the unit cell. Potential energy conformational analysis was applied to polyurethanes for the first time. The results point to a fully extended poly(MDI/butandiol) chain linked to its neighbors in a stabilizing two-dimensional hydrogen bonding network.

This work was expanded to the polyurethanes prepared using the C_2 - C_8 homologous series of diols. The even diol series (except C_2) adopt fully extended structures like that for the C_4 polymer. In contrast the odd diol series adopt higher energy contracted conformations, probably in order to form intermolecular hydrogen bonds. The odd series are less crystalline, as might be expected since the lower energy extended forms can crystallize more easily. Crystallinity is part of the driving force for phase separation, and hence the results correlate with the better properties generally seen for the even diol series of polyurethanes.
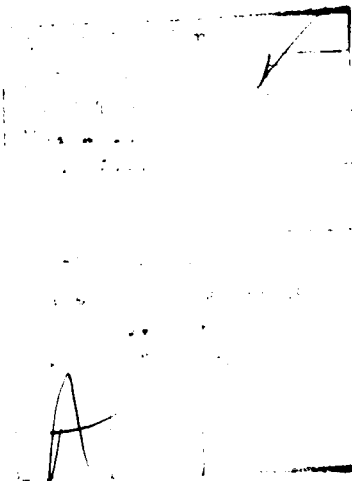
INTRODUCTION

For the last six years we have used x-ray diffraction and other physical chemical methods to determine the physical structures of these materials, and have thereby extended our understanding of their structure-property relationships. Our main concern has been to determine the structures of the hard domains. Polyurethane elastomers are block copolymers consisting of alternating hard (urethane) and soft (usually polyester or polyether) segments that are respectively below and above their glass transition temperatures. The elastomeric properties derive from phase separation, such that the hard segments form discrete domains (1,2) in the matrix of the soft segments: the hard domains serve as virtual crosslinks and also as filler particles. Polymers of this type include thermoplastic and cast polyurethane elastomers, and also Spandex fibers, and range in properties from soft, highly extendable materials to hard compositions, more like conventional plastics.

In our research we have been mainly concerned with the important group of polyurethanes in which the hard domains are prepared from 4,4'-diphenylmethane diisocyanate (MDI) with a linear diol as the chain extender:

$$— [— \{—OCONH \langle \overline{} \rangle CH_2 \langle \overline{} \rangle NHCO \cdot O — (CH_2)_x—\}_n —\text{soft segment}—]_{n'}—$$
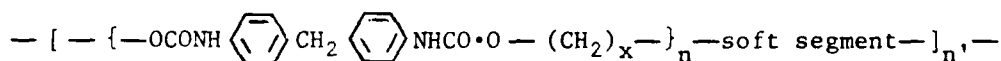
The soft segment polymer has generally been poly(tetramethylene adipate) (PTMA) but we have also looked at some preparations that used copoly-(ethylene oxide/butandiol oxide). A typical polymer that we have studied is prepared from MDI, butandiol (BDO), and PTMA ($M_n \approx 2000$) in the molar ratios 6:5:1 respectively, and contains approximately equal proportions of hard and soft segments.

The MDI/diol polyurethanes form the basis for many commercial preparations (the latter are often more complex, due to added features such as covalent cross-linking) and their structures have been the subject of extensive study. In these copolymers, the hard segments can crystallize, and the development of crystallinity is thought to be an important feature of the virtual cross-linking. (3) It is also a factor in the phase separation process, (4,5) which in turn is a major determinant of the bulk properties. A detailed knowledge of how polyurethanes crystallize, and the role of crystallinity in phase separation, will lead to considerable improvement in our understanding of their structure-property relationships. Our results will also have implications for the structure of other polyurethane materials, notably foams and adhesives, and for block copolymers in general.

Studies of the mechanical and thermal properties of MDI/diol polyurethanes have shown that they depend considerably on the chemical structure. (6) Naturally they depend on the relative proportions of hard and soft segments, and on the average segment lengths. In addition, it is found that the properties vary with the length of the diol chain extender (i.e., the number of CH_2 groups, x), when all other factors are held constant. (7-9) As will be seen below, we have shown that the hard domains prepared from odd and even diol chain extenders have different types of crystal structures, i.e., the hydrogen bonding and other molecular interactions are different, and this can be correlated with the reported zigzagging of the properties from odd to even along the homologous series of chain extenders.

There has been considerable work on the physical structures of these systems using a wide variety of techniques, including small and

wide angle x-ray diffraction, electron microscopy, infrared and NMR spectroscopy, and dynamical-mechanical and thermal analysis. The general conclusion has been that the hard and soft segments form separate domains, and that the properties are critically dependent on the extent of phase separation. We have been concerned with the th ee-dimensional arrangement of the chains in the crystalline (or paracrystalline) hard domains. Further description of the structure is in terms of the size of the hard domains, the nature of the boundary regions, and the extent of residual phase mixing.

Previous to our work, the most detailed proposals for the structure of the hard segments were due to Bonart and co-workers. (10-12) Stretched annealed films of the MDI/butandiol/PTMA elastomers showed a single Bragg reflection that could be assigned to the hard domains: an off meridional at $d \sim 7 \cdot 9 Å$ inclined at $\sim 30°$ to the meridian. (The soft segments were amorphous following annealing at temperatures above their melting point.) Bonart suggested that this reflection arose due to staggering of adjacent chains along the fiber axis, in order to form straight $C = O \cdots H - N$ hydrogen bonds between the urethane groups, as shown in fig. 1(a). This staggering leads to Bragg planes inclined with respect to the chain axis that could be responsible for the observed reflection.

Bonart's model, however, is simply a schematic, and takes no account of the stereochemistry of the molecules. Figure 1(b) shows the model derived in this laboratory (see below), based on more detailed x-ray patterns and the structures of model 4,4'-diphenylmethane diurethane compounds. (13-15) The chains are fully extended and are linked by $C = O \cdots H - N$ hydrogen bonds in both directions perpendicular to their
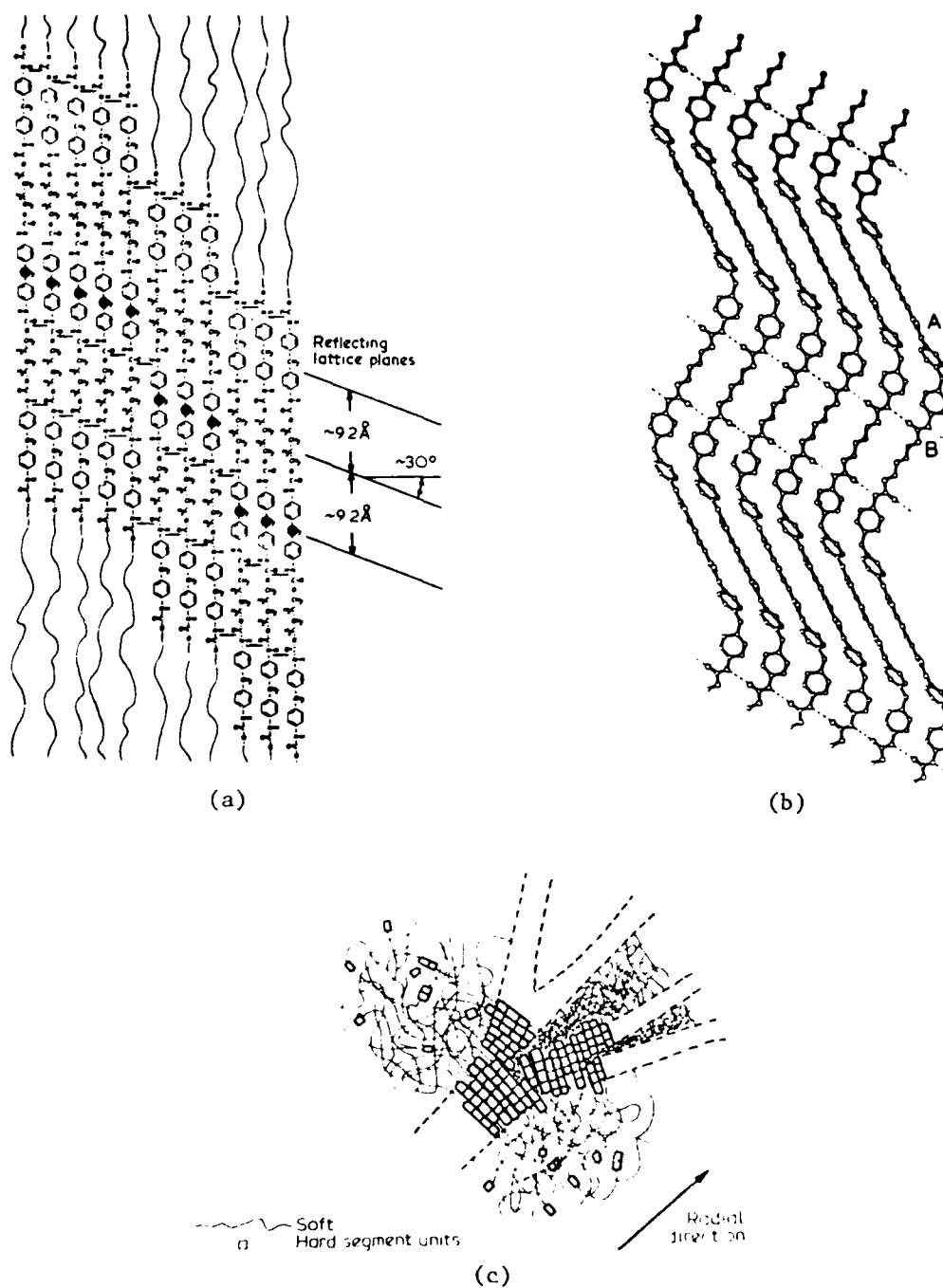
(a)

(b)

(c)

Fig. 1

(a) Staggered chain structure for poly(MDI/butandiol) proposed by Bonart et al. (11)

(b) Stereochemical model for the same polymer proposed by Blackwell and Gardner. (13)

(c) Proposed hard domain structure in spherulitic morphology (Fridman and Thomas). (17)

axes. The hydrogen bonding and the stacking interactions of the diphenyl-
methane groups lead to a highly stable crystalline structure.

A spherulitic morphology has been reported for polyurethane elastomers
based on transmission electron microscopy. (16,17) Efforts to resolve
the actual domain structure are made difficult by the problems of staining
MDI/diol/polyester or polyether specimens. Koutsky et al (18) reported
the existence of hard domains that were 30 – 500Å in diameter. Later
a fibrous or lamellar morphology was observed by Schneider et al, (19)
who proposed that this was due to lateral aggregation of the chains,
where the width of the lamellae would be determined by the average hard
segment length. This view was also taken by Fridman and Thomas, (17)
who observed fibrous (lamellar) structures in MDI/butenediol/poly(propylene
oxide) specimens. (In these specimens the butenediol units can be stained
with OsO_4.) The model proposed by the latter authors for the hard domains
is shown in fig. 1(c). Small angle analyses of polyurethane elastomers
frequently show a single maximum at $d \simeq 200$Å, which is assigned to the
separation between the hard domains. (20-24) Calculations based on
a lamellar morphology have indicated a boundary region of 10 – 20Å between
the hard and soft domains.

Most physical studies, including DSC and mechanical property data,
suggest that the phase separation is not complete, i.e., there is residual
phase mixing. (23-28) Many of the short hard segments consisting of
only one or perhaps two MDI units may not be phase separated, (21) and
this is likely to apply also to some of the longer chains due to stereo-
chemical restrictions. Infrared spectroscopy for an MDI/butandiol/polyester

specimen by Cooper and co-workers (29) showed that only approximately

60% of the carbonyl groups are involved in hydrogen bonding as would

occur in the crystalline hard domains. The remainder would correspond

to the non-phase separated hard segments and some of the carbonyls in

the boundary regions.

PROGRESS REPORT

Summary

1. A new structure has been developed for the structure of MDI/butandiol hard segments, based on the following approaches.

   a) Single crystal structures of two model 4,4'-diphenylmethane di- urethane compounds were solved in this laboratory. These showed the basic features of the monomer conformation and the molecular stacking and hydrogen bonding.

   b) Better quality x-ray patterns were obtained for the hard segments, from which a unit cell was determined.

   c) Conformational analysis was applied to polyurethanes for the first time, and the fiber repeats were calculated for the various energy minima.

2. The above research was expanded to study the structures of MDI/diol hard segments prepared using the $C_2 - C_8$ series of diol chain exten- ders.

   a) The even diol series (except C_2) crystallize in fully extended minimum energy conformations analogous to that for the C_4-polymer.

   b) The odd diol series do not crystallize in the fully extended structures but rather adopt higher energy contracted conforma- tions, probably in order to optimize their hydrogen bonding networks.

   c) The first member of the series, the C_2-polymer, also has a contracted conformation. This may be because the $(CH_2)_2$ chain is too short to allow adequate packing of the diphenylmethane units in the fully extended conformation.

d) There are indications of polymorphic structures for the C_8 and C_4-polymers.

e) The results can be correlated with the zigzag behavior seen for the bulk properties along the homologous series.

3. The structure and morphology of the soft segment polymer was investigated in order to be able to identify the features of both hard and soft segments in the data for the copolymer.

Personnel

Professor John Blackwell		Principal Investigator
Dr. Kenncorwin H. Gardner	1976-77	Postdoctoral Associate
Dr. Mahedev R. Nagarajan	1978-82	Postdoctoral Associate

There were no graduate students supported by this project. However, the following students acknowledged the support of these grants for their thesis work.

Kam Minke	Ph.D.	1978	"The Structures of Chitin and Poly(tetramethylene adipate)"
Todd B. Hoitink	M.S.	1981	"The X-ray Studies of the Structure of Polyurethane Elastomers"

PUBLICATIONS

1. "The Structure of the Hard Segments in Polyurethane Elastomers",
   by J. Blackwell and K.H. Gardner, Polymer 20, 13 (1979).

2. "X-ray Studies of the Structure of Polyurethane Hard Segments",
   by J. Blackwell and M. Ross, J. Polymer Sci., Polymer Letters Edns.
   17, 447 (1979).

3. "Polymorphic Structures of Poly(tetramethylene Adipate), by R. Minke
   and J. Blackwell, J. Macromol. Sci.-Phys. B16, 407 (1979).

4. "Structure of Dimethyl 4,4'-Methylenebis(phenylcarbamate): a Model
   for the MDI Units in Polyurethane Hard Segments", by K.H. Gardner
   and J. Blackwell, Acta Crystallogr. B36, 1972 (1980).

5. "Single Crystals of Poly(tetramethylene Adipate)", by R. Minke
   and J. Blackwell, J. Macromol. Sci.-Phys. B18, 233 (1980).

6. "The Structure of Bis(4-hydroxyl) 4,4'-Methylene Bis(phenylcz   ‑
   mate): a Model Compound for Diol-linked MDI Units in Polyur‹   ane
   Elastomers", by P.G. Forcier and J. Blackwell, Acta Crystallc
   B37, 286 (1981).

7. "Conformational Analysis of Poly(MDI/butandiol) Hard Segment. ‑
   Polyurethane Elastomers", by J. Blackwell and M.R. Nagarajan,
   Polymer 22, 202 (1981).

8. "Structure of Polyurethane Elastomers. X-ray Diffraction and Con-
   formational Analysis of MDI-propandiol and MDI-ethylene Glycol
   Hard Segments", by J. Blackwell, M.R. Nagarajan, and T.B. Hoitink,
   Polymer 22, 1534 (1981).

9. "The Structure of the Hard Segments in MDI/diol/PTMA Polyurethane
   Elastomers", by J. Blackwell, M.R. Nagarajan, and T.B. Hoitink,
   in Urethane Chemistry and Applications (ed. K.N. Edwards), A.C.S.
   Symp. Ser. 172, 179 (1981).

10. "Structure of Polyurethane Elastomers: Effect of Chain Extender
    Length on the Structure of MDI/diol Hard Segments", by J. Blackwell,
    M.R. Nagarajan, and T.B. Hoitink, Polymer 23, 950 (1982).

INVITED LECTURES

1. "The Structure of the Hard Segments in MDI/diol/PTMA Polyurethane
   Elastomers", by J. Blackwell, M.R. Nagarajan, and T.B. Hoitink,
   at Amer. Chem. Soc. Meeting, Las Vegas, Nevada, August 1980.

2. "The Structure of Polyurethane Elastomers", by J. Blackwell, at
   Gordon Conference on Polymers, Ventura, California, January 1981.

INVITED LECTURES (cont'd)

3. "The Structure of the Hard Segments in Polyurethane Elastomers",
   by J. Blackwell, M.R. Nagarajan, and T.B. Hoitink, at IUPAC MACRO
   82 Symposium, Amherst, Massachusetts, July 1982.

CONTRIBUTED PAPERS

1. "The Structure of the Hard Segments in Polyurethane Elastomers",
   by J. Blackwell, K. H. Gardner, and M. Ross, at Amer. Phys. Soc.
   Meeting, Chicago, Illinois, March 1980.

2. "The Structure of the Hard Segments in Polyurethane Elastomers",
   by M.R. Nagarajan, T.B. Hoitink, and J. Blackwell, at Amer. Phys.
   Soc. Meeting, New York, New York, March 1981.

DETAILED REPORT

1. Model Compounds

Methanol-capped MDI (MeMMeI) and butandiol capped MDI (HOBMBOH)
were crystallized from methanol solutions and their structures were
solved by single crystal direct methods and refined by least
squares. (15,30) The molecular conformations and packing of these
compounds is shown in fig. 2. These structures were solved to serve
as models for the conformation, packing, and hydrogen bonding of the
MDI/diol hard segments (no structures of 4,4'-diphenylmethane diurethanes
had been published previously). We have also crystallized propanol-
capped MDI, but have not attempted to solve this structure as yet. We
are trying to crystallize the larger compound, butandiol-MDI-butandiol-
MDI-butandiol, but have not been successful so far. The compounds were
generously supplied by Drs. C.W. Wilkes and C.S. Schollenberger of
B.F. Goodrich Co., Brecksville, Ohio.

The relevant details of the MeMMeI structure (15) are summarized
below.

a) The central $C-\hat{C}H_2-C$ bridge angle is $114 \cdot 6°$.

b) The conformation is not symmetrical, despite the chemical symmetry,
   i.e., the two ends of the molecule, designated A and B in fig. 2(a)
   are physically different. Nevertheless, the mutual orientation of
   the phenyl groups (A and B) is $90 \cdot 0°$, corresponding to minimum over-
   lap of the π-orbitals.

c) The urethane groups are planar (including the terminal carbon) and
   are oriented at $39 \cdot 4°$ (A) and $10 \cdot 2°$ (B) to their adjacent phenyls.

d) The molecules are stacked along the a axis, and this stacking is prob-
   ably analogous to the structure of the polymer. The hydrogen bonding
   of the A-urethanes occurs within the stack of molecules, with the
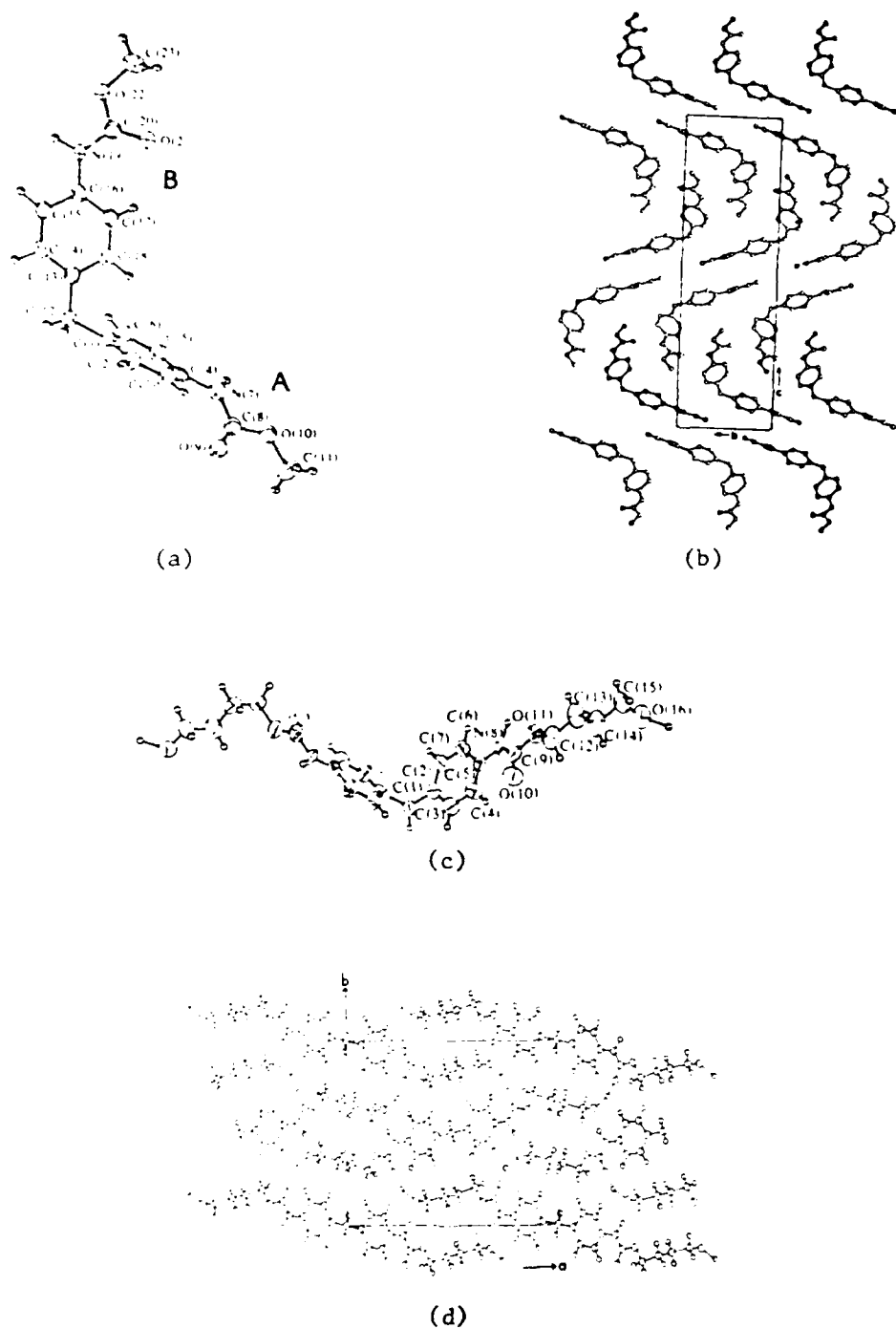   B-urethanes bonded to adjacent stacks.

(a)

(b)

(c)

(d)

Fig. 2

(a) Conformation of MeMMeI. (15) The molecule is not symmetrical and the two halves of the molecule are designated A and B.

(b) Molecular packing of MeMMeI (15)

(c) Conformation of HOBMBOH (30)

(d) Molecular packing of HOBMBOH (30)

The HOBMBOH structure (30) was solved in order to investigate the urethane-diol conformation. As can be seen in fig. 2(d), the packing is quite different from that for MeMMeI, probably as a consequence of the need to hydrogen bond the hydroxyls. The important features of the structure are as follows:

a) The central $C-CH_2-C$ bridge angle is 105·2° and the phenyl-phenyl orientation is 98°, which gives some idea of the tolerated range in these parameters. [The structures of three diphenyl methanes (31) found in the literature have conformations more similar to MeMMeI.] The molecular conformation is symmetrical with a phenyl-urethane orientation of 13·2°.

b) The terminal butandiol $-C_4-O$ chain is planar but is oriented gauche to the urethane group.

c) The molecules are stacked along the a axis but are hydrogen bonded along the b axis, i.e., perpendicular to the stacks, giving a sheet-like structure. There are no urethane-urethane hydrogen bonds.

As will be seen, these structures have generated considerable information with regard to the polymer structures. The structure of a second form of methanol-capped MDI (MeMMeI') has been solved by Hocker and Born (32) at Bayer AG, Leverkusen, although a full structure has not been published to date. (We also crystallized this polymorph, but did not proceed further when their preliminary report was published.) The MeMMeII structure is similar to that of HOBMBOH in that the hydrogen bonding is in sheets perpendicular to the stacked molecules, and is of a type that could not occur for the polymer chains.

2. Proposed Structure of Poly(MDI/butandiol) Based on MeMMeI

The model for poly(MDI/butandiol) in fig. 1(b) was predicted (13) assuming that the conformation and stacking of the monomers would be the same as in the MeMMeI structure. (This was done before the improved x-ray patterns became available; see below.) Space does not permit a full discussion of the packing possibilities, but it is clear that in the polymer the stacking of the diphenalmethane units must be similar to that for MeMMeI in order to allow for hydrogen bonding of the urethanes. It should also be noted that the molecules are fortuitously crystallized almost end-to-end with a center of symmetry between them [see the shaded pair of molecules in fig. 2(b)]. All that is necessary is to link these by a $-CH_2-CH_2-$ chain to form a dimer repeat; the polymer chain is then built up by translation. We assumed a planar zigzag conformation arranged trans to the urethane group. As will be seen, this is the minimum energy conformation. The MeMMe molecules are linked by hydrogen bonds in stacks along the a axis. This bonding and stacking is retained in the postulated polymer model: fig. 1(b) is a view of the stacked polymer chains perpendicular to the original a axis. Thus the sheet of chains in fig. 1(b) is lifted straight from the MeMMeI structure, with simply the addition of a trans $-CH_2-CH_2-$ unit. The packing in the third dimension was determined approximately by stacking such sheets to form straight $C = O \cdots H - N$ hydrogen

bonds. This yields a structure with a triclinic unit cell with approximate dimensions $a = 5 \cdot 2 \text{Å}$, $\underline{b} = 4 \cdot 8 \text{Å}$, $\underline{c} = 35 \cdot 0 \text{Å}$, $\alpha = 121°$, $\beta = 116°$, $\gamma = 83 \cdot 5°$, and space group $P\bar{1}$.

The model is attractive because of the stability given to it by the hydrogen bonding network and the stacking of the diphenyl methanes. The chains are staggered as proposed by Bonart $\underline{et}$ $\underline{al}$ (11) and the tilted base plane of the unit cell would give rise to $\overline{00\ell}$ reflections inclined at approximately the correct angle to the meridian. When first conceived the model was totally hypothetical, but it can now be seen to be approximately correct as a result of further x-ray and conformational analyses.

3. X-ray Diffraction Patterns of Poly(MDI/butandiol)

After the above packing model was derived, we were able to obtain better quality x-ray patterns for the hard segments. Film specimens of MDI/diol/PTMA (M. Wt. 2000) were prepared in the mole ratios 6:5:1 and 7:6:1 for the homologous series of diols from C_2 to C_8; the specimens were synthesized by Dr. C.S. Schollenberger. For the butandiol (C_4) polymer the films were stretched 700% at 130°C over a period of a week. The x-ray fiber diagram (14) shows twelve reflections that can be assigned to the hard phase. (We can be sure of this from our knowledge of the diffraction characteristics of both crystalline forms of PTMA.) (33) The twelve reflections can be indexed by a triclinic unit cell with dimensions $a = 5 \cdot 05 \text{Å}$, $b = 4 \cdot 67 \text{Å}$, $c = 37 \cdot 9 \text{Å}$, $\alpha = \beta = 116°$, and $\gamma = 83 \cdot 5°$. The similarity between this unit cell and that proposed from the model building is striking, and it is clear that our proposals are along the right lines.

However, a criticism of our unit cell from the x-ray work is that it gives a calculated density of $1 \cdot 57$ gm/cm^3, which is relatively high. We have recently been able to measure the density of the hard segment homopolymer: the observed density is $\sim 1 \cdot 3$ gm/cm^3, and the difference is too great to be due to incomplete crystallinity. We cannot find another unit cell that satisfactorily indexes the observed reflections. However, we now have evidence that suggests that three of the reflections may be due to a second polymorphic form. The remaining nine reflections are all indexed $h0\ell$, which means that the $\underline{b}$ dimension is not defined. If $a = b = 5 \cdot 1 \text{Å}$, the nine reflections would be multiply indexed as $h0\ell$ and $\overline{0k\ell}$ ($h = k$); these dimensions give a calculated density of $1 \cdot 42$ gm/cm^3, which is more reasonable. The research proposed below includes a thorough investigation of polymorphisms for the homologous series of MDI/diol hard segments.

4. Conformational Analysis

We have used minimum energy conformational analysis to predict the conformation of the poly(MDI/diol) chains. (34) This is the first time that such analyses have been applied to polyurethanes. Standard bond lengths and angles were used for the aromatic and aliphatic groups; for the urethane groups we surveyed nineteen urethane structures in the crystallography literature and generated the average values. The potential energy calculation included terms for non-bonded, electrostatic, torsional,

and bond angle deformation. The main conclusions with respect to the poly(MDI/butandiol) chain were as follows:

a) The phenyl groups are mutually perpendicular, as was found for the model compounds MeMMeI.

b) The phenyl and urethane groups are also predicted to be perpendicular, ($\psi = 90°$) compared to $\psi = 10\cdot2$, $13\cdot2$, and $39\cdot4°$ in the model compounds. The observed conformations are $3 - 6$ kcals/mole higher than the energy minimum. This gives an idea of the energy due to packing forces and hydrogen bonding. In addition there is the possibility of π-orbital overlap between the phenyl and urethane groups. A similar problem is encountered in predicting the structure of Kevlar. (35,36) However, for the diphenylmethane diurethane unit, the overall length is relatively insensitive to the value of ψ.

c) The butandiol unit must be in the planar all-<u>trans</u> conformation and arranged <u>trans</u> to the urethanes, otherwise the observed fiber repeat of $37\cdot9\overset{\circ}{A}$ cannot be achieved.

From these calculations, the conformation of the poly(MDI/butandiol) chain can be predicted, and this has a similar appearance to that in fig. 1(b), except that the fiber repeat is $37\cdot9\overset{\circ}{A}$. We have also started a packing analysis to see how the chain will fit into the unit cell. This analysis uses the Williams packing analysis (PACK) programs, (37) and refines the structure in terms of the conformational angle ψ and the orientation of the chain about its axis. Although this work is not complete, it is immediately apparent that the <u>b</u> dimension of $4\cdot67\overset{\circ}{A}$ is too short for acceptable packing, but that this can be achieved with $a = b \simeq 5\cdot1\overset{\circ}{A}$. We propose to continue this analysis, coupled with linked atom least squares refinement against the x-ray data. Conformational analysis has also been carried out for MDI/diol hard segments with other diol chain extenders. Some of the results of this work are included in the next section.

## 5. Poly (MDI/diol) Structures for the $C_2 - C_8$ diol Series

We have extended the above x-ray and model building studies to consider the structures of MDI/diol hard segments prepared from other chain extenders, (38-40) specifically to see how the structures vary across the homologous series of diols from $C_2 - C_8$. X-ray fiber diagrams were obtained for films of the $C_3 - C_6$ polymers stretched 700% at 130°C. For the C_2, C_7, and C_8-polymers this approach was not successful and specimens were prepared by stretching 400% at room temperature. Schematics of the x-ray patterns for the series are shown in fig. 3. The fiber repeats for the MDI/diol polymers are shown in Table 1.
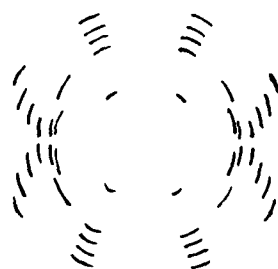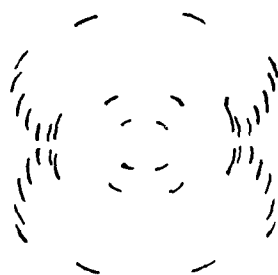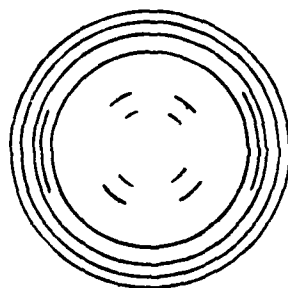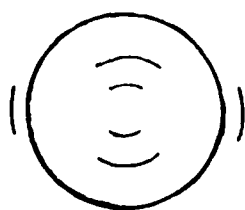
Fig. 3 Schematics of the x-ray diffraction patterns of oriented films of:

(a) MDI/butandiol/PTMA
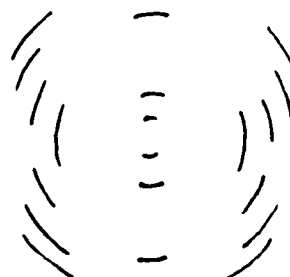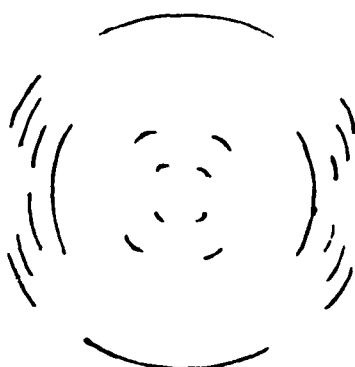(b) MDI/hexandiol/PTMA
(c) MDI/octandiol/PTMA

N.B. (a), (b), and (c) all show the characteristics of extended conformations.
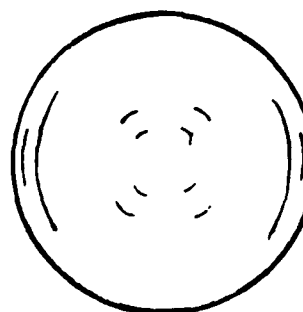
(d)

(e)

(f)

(g)

Fig. 3 (continued)

Schematics of the x-ray diffraction patterns of oriented films of:

        (d) MDI/ethylene glycol/PTMA
        (e) MDI/propandiol/PTMA
        (f) MDI/pentandiol/PTMA
        (g) MDI/heptandiol/PTMA

N.B. (d), (e), (f), and (g) all show the characteristics of contracted conformations.

Table 1

Fiber repeats for poly(MDI/diol) homologous series

$-(CH_2)_x-$ x	Fiber Repeat (per monomer) Å	Conformation
2	$15 \cdot 0 \pm 0 \cdot 2$	Contracted
3	$16 \cdot 2 \pm 0 \cdot 2$	Contracted
4	$18 \cdot 9_5 \pm 0 \cdot 2$	Extended
5	$18 \cdot 6 \pm 0 \cdot 2$	Contracted
6	$20 \cdot 8_5 \pm 0 \cdot 2$	Extended
7	$20 \cdot 7 \pm 0 \cdot 4$	Contracted
8	$22 \cdot 8 \pm 0 \cdot 4$	Extended

From table 1 it can be seen that the polymers fall into two classes. Prediction of the fiber repeats by conformational analysis shows that the C_4, C_6, and C_8-polymers crystallize in the minimum energy, fully extended conformations. The crystal structures of the C_6 and C_8-polymers appear to be analogous to that for the C_4-polymer in fig. 1(b), with simply the addition of further trans $-CH_2-CH_2-$ units. The other polymers, however, are less crystalline, and all have fiber repeats significantly shorter than those predicted for the fully extended chains. The length of the diphenylmethane diurethane unit is not very sensitive to conformation, and hence the reduction in the fiber repeat must occur in the diol section of the chain, i.e., there must be some gauche C_2 groups. The conformational analysis shows that in all cases the observed fiber repeat is given by a contracted chain with two gauche torsional angles in the diol section, the remainder being trans. For the C_2-polymer, this requires the gauche$^+$ - trans - gauche$^-$ conformation, which is shown in fig. 4(a). The other polymers have longer diol sections and this leads to ambiguity: for the C_3-polymer both the trans - gauche$^+$ - gauche$^+$ trans and gauche$^+$ - trans - trans - gauche$^+$ conformations match the observed fiber repeat of $16 \cdot 2$Å. These two conformations are shown in fig. 4(b); the former conformation is of slightly lower energy. In this regard, the structure of the model compound HOBMBOH favors the former conformation. In HOBMBOH the diol units are planar, but are gauche to the urethane; the separation of the appropriate CH_2 groups predicts a fiber repeat of $16 \cdot 34$Å for the C_3-polymer. Similar agreement is obtained for the repeats of the C_5 and C_7-polymers.

All of the polymers adopt staggered triclinic structures, except for the C_2 and C_3-polymers. Here the x-ray patterns show meridional reflections, indicating that the unit cells are monoclinic or orthorhombic and the base planes are perpendicular to the chain axes, i.e, adjacent chains are in register rather than staggered. Further work is necessary to find the explanation for this. However, it is not unusual for the first one or two members of a homologous series to be exceptions to the general behavior. It may be that the C_2 and C_3-diols are too short to allow for adequate packing of the large diphenylmethane units in the staggered arrays. This may also explain why the C_2-polymer has a contracted rather than extended conformation.
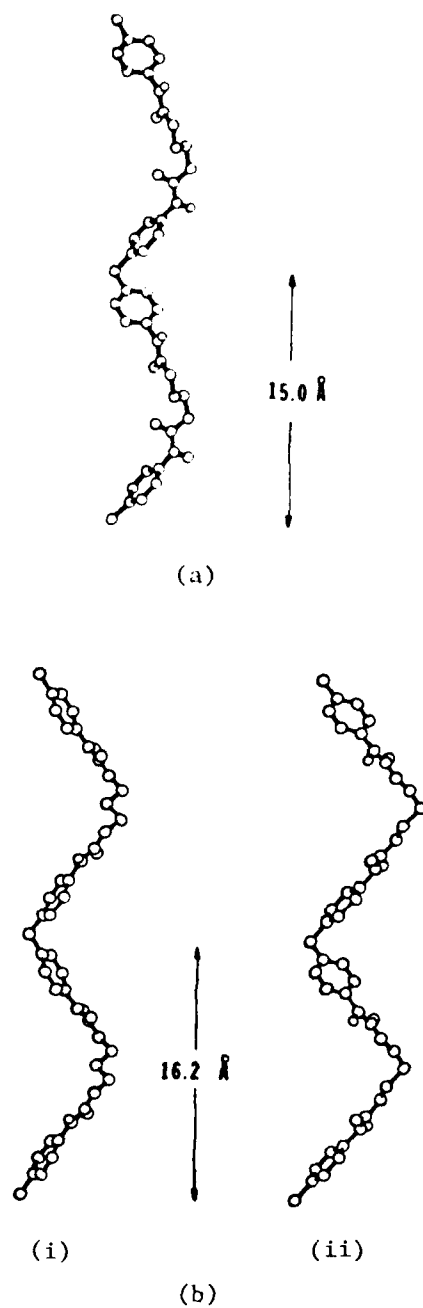
(a)

(i)   (ii)

(b)

Fig. 4

(a) Contracted conformation of poly(MDI/ethylene glycol) with
    gauche$^+$ - trans - gauche$^-$ diol section. (38)

(b) Two possible contracted conformations for poly(MDI/propandiol). (38)
    (i) gauche$^+$ - trans - trans - gauche$^+$
    (ii) trans - gauche$^+$ - gauche$^+$ - trans

We have already referred to evidence for polymorphism in some of these structures. The best evidence for this comes from the C_8 polymer where there is sometimes evidence for a small proportion of a contracted form that increases in content with annealing. There is also evidence for an apparently contracted form for the C_4 polymer that decreases in content on annealing at 130°C. Nevertheless, the predominant form in the unoriented and oriented films of these two polymers is the extended conformation. Polymorphism is a common phenomenon in polymer structures and it should not be surprising that it occurs for these polyurethanes.

Examination of fig. 1(b) shows a simple reason for the different behavior of the odd series of polymers. In the even polymers, the carbonyls point to opposite sides of the planar zigzag, which leads to the formation of straight hydrogen bonds between the staggered chains. When we have an odd diol extender, however, the carbonyls point to the same side of the fully extended chains, and this would lead at best to the formation of highly non-linear hydrogen bonds. Thus it is not surprising that the odd diol polymers take up a contracted conformation in order to optimize their hydrogen bonding network.

These structures can be correlated with the reported zigzagging of the bulk properties of the elastomers as one goes from odd to even diols along the series, (7-9) with the better properties occurring for the even series. The even diol polymers crystallize in the minimum energy conformation with a very efficient molecular packing. In contrast, the odd diol series have to crystallize in a higher energy conformation, for which the packing is probably less efficient (further work is necessary to be sure of the latter point, but it appears likely). The development of crystallinity is an important factor in the phase separation which in turn determines many of the properties. Further work is necessary to build on these correlations in order to understand the relationships between the physical structures and the bulk properties.

6. Diffraction Data for PTMA

The above x-ray studies of the hard segment structures were done mainly on specimens in which the soft segments are amorphous, due to annealing at a temperature above the soft segment melting temperature. Given the small amount of x-ray data for the hard segments, it is essential to be sure that none of the reflections are due to residual soft segment crystallinity. For this reason we have studied the diffraction characteristics of the soft segment polymer, PTMA. This work is described in detail in reference 33. The basic conclusion is that there are two crystalline forms of PTMA, designated α- and β-. We were able to establish the unit cells of these polymers from the x-ray patterns of oriented films of the homopolymer, augmented by electron diffraction patterns of normal and epitaxially grown single crystals. These data were utilized in our studies of the C_6, C_7, and C_8-polymers, which were stretched at room temperature and showed the diffraction characteristics of both the hard and soft segments.

REFERENCES

1. Allport, D.C. and Mohajer, A.A., in Block Copolymers (ed. D.C. Allport), Wiley-Interscience, New York (1973).

2. Cooper, S.L. and Tobolsky, A.V., J. Appl. Polymer Sci. 10, 1837 (1966).

3. Van Bogart, J.W.C., Lilaonitkul, A., and Cooper, S.L., in Multiphase Polymers (eds. S.L. Cooper and G.M. Estes), A.C.S. Adv. Chem. Ser. 176, 3 (1979).

4. Krause, S., in Block and Graft Copolymers (eds. J.J. Burke and V. Weiss), Syracuse University, Syracuse, New York (1973), p. 143.

5. Meier, D.J., in Block and Graft Copolymers (eds. J.J. Burke and V. Weiss), Syracuse University, Syracuse, New York (1973), p. 105.

6. Noshay, A. and McGrath, J.E., "Block Copolymers. Overview and Critical Survey", Academic Press, New York (1977).

7. Bonart, R., Morbitzer, L., and Rinke, H., Kolloid Zeit-Z. Polym. 240, 807 (1970); Bleijenberg, A.C.A.M., Heikens, D., Meijers, A., and van Reth, P.H., Brit. Polymer J. 4, 125 (1972).

8. Critchfield, F.E., Koleske, J.V., Magnus, G., and Dodd, J.L., J. Elasto-plast. 4, 22 (1972).

9. Kajiyama, T. and MacKnight, W.J., Macromolecules 2, 254 (1969).

10. Bonart, R., J. Macromol. Sci.-Phys. B2, 115 (1968).

11. Bonart, R., Morbitzer, L., and Hentze, G., J. Macromol. Sci.-Phys. B2, 337 (1968).

12. Bonart, R., Morbitzer, L., and Müller, E.H., J. Macromol. Sci.-Phys. B9, 447, (1974).

13. Blackwell, J. and Gardner, K.H., Polymer 20, 13 (1979).

14. Blackwell, J. and Ross, M., J. Polymer Sci., Polymer Lett. Edns. 17, 723 (1979).

15. Gardner, K.H. and Blackwell, J., Acta Crystallogr. B36, 1972 (1980).

16. Samuels, S.L. and Wilkes, G.L., Polymer Letters 9, 761 (1971); Wilkes, G.S., Samuels, S.L., and Crystal, G., J. Macromol. Sci.-Phys. B10, 203 (1974).

17. Fridman, I.D. and Thomas, E.L., Polymer 21, 388 (1980).

18. Koutsky, J.S., Hein, N.V., and Cooper, S.L., J. Polymer Sci. (B) 8, 352 (1970).

19. Schneider, N.S., Desper, C.R., Illinger, J.L., King, A.O., and Barr, D., J. Macromol. Sci.-Phys. B11, 527 (1975).

20. Bonart, R. and Müller, E.H., J. Macromol. Sci.-Phys. B10, 177 (1974).

21. Bonart, R. and Müller, E.H., J. Macromol. Sci.-Phys. B10, 345 (1974).

22. Wilkes, C.E. and Yusek, C.S., J. Macromol. Sci.-Phys. B7, 157 (1973).

23. Schollenberger, C.S., in Multiphase Polymers (eds. S.L. Cooper and G.M. Estes), A.C.S. Adv. Chem. Ser. 176, 87 (1979).

24. Ophir, Z.H. and Wilkes, G.L., in Multiphase Polymers (eds. S.L. Cooper and G.M. Estes), A.C.S. Adv. Chem. Ser. 176, 53 (1979).

25. Clough, S.B. and Schneider, N.S., J. Macromol. Sci.-Phys. B2, 553 (1968).

26. Van Bogart, J.W.C., Bluemke, D.A., and Cooper, S.L., Polymer 22, 1428 (1981).

27. Hespe, H., Meisert, E., Eisele, U., Morbitzer, L., and Goyert, W., Kolloid Zeit.-Z. Polym. 250, 797 (1972).

28. Huh, D.S. and Cooper, S.L., Polym. Engr. Sci. 11, 369 (1971).

29. Seymour, R.W., Estes, G.M., and Cooper, S.L., Macromolecules 3, 579 (1970); Estes, G.M., Seymour, R.W., and Cooper, S.L., Macromolecules 4, 453 (1971).

30. Forcier, P.G. and Blackwell, J., Acta Crystallogr. B37, 286 (1981).

31. Chaudhari, B. and Hargreaves, A., Acta Crystallogr. 9, 793 (1956); Svardstrom, J.W., Duvall, L.A., and Miller, D.P., Acta Crystallogr. B28, 2510 (1972); Whittaker, E.J.W., Acta Crystallogr. 6, 714 (1953).

32. Hocker, J. and Born, L., J. Polymer Sci., Polymer Lett. Edns. 17, 723 (1979).

33. Minke, R. and Blackwell, J., J. Macromol. Sci.-Phys. B16, 407 (1979); Minke, R. and Blackwell, J., J. Macromol. Sci.-Phys. B18, 233 (1980).

34. Blackwell, J. and Nagarajan, M.R., Polymer 22, 202 (1981).

35. Hummell, J.P. and Flory, P.J., Macromolecules 13, 479 (1980).

36. Tashiro, K., Kobayashi, M., and Tadokoro, H., Macromolecules 10, 413 (1979).

LMED
8